A STUDY OF THE REDUCTION OF PERMANGANIC ACID BY MANGANESE DIOXIDE.

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A Dissertation Presented to the Board of University Studies of the Johns Hopkins University for the Degree of Doctor of Philosophy.

by

Horace G. Byers.

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Acknowledgement.

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Introduction.

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Work upon the reaction between permanganic acid and peroxides was begun several years ago in this laboratory by Messrs. Morse and Allen. An outline of the literature upon the subject is to be found in Allen's Dissertation.(1)

They found, contrary to the theory of Schoenbein,(2) that antozonides, compounds which being heated with hydrochloric acid yield chlorine and not hydrogen dioxide, were capable of mutual decomposition and this led them to the suspicion that the well-known instability of potassium permanganates ought to be ascribed to a similar cause and that the long known decomposition of permanganic acid by certain peroxides might also take place with manganese dioxide. This reaction is vaguely referred to by Thenard,(3) who says that manganese dioxide may act upon permanganate either as a reducing agent, in which case the dioxide is changed to a manganate, or its action may be catalytic in which case oxygen is evolved. The investigation of this subject was taken up by Morse

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(1) Johns Hopkins Dissertations. 1892.
(2) Ann., 108,172.
(3) Compt. Rend. 42, 382.

and Hopkins and has been continued for several years.

The results that have been arrived at are in part here summarized.

Manganese dioxide decomposes permanganic acid and the permanganates in accordance with the following equation:

$$2H\,Mn\,O_4 + Mn\,O_2 = 3\,Mn\,O_2 + 3O + H_2O.$$

This is evidenced by the fact that if permanganate is decolorized as by the above reaction the loss of available oxygen is in the proportion indicated by the equation,(1) that is three-fifths of the active oxygen is evolved. That instability of permanganate solutions is to be ascribed to this reaction is shown by the fact that solutions carefully freed from oxide have remained perfectly constant during long periods of time and in varying conditions of temperature.(2)

Permanganic acid is slowly reduced in the direct sunlight even in the absence of the oxides. The evidence on this point was furnished by duplicate experiments where solutions otherwise identical were

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(1) Am. Chem. Jour., vol.XVIII

(2) Am. Chem. Jour., vol.XVIII.

placed one in the sunlight the other in darkness. The first decreased in concentration, the second did not.(1)

The reaction expressed above is much hastened by the addition of acid and by increase either of the strength of the solution of permanganic acid or of the proportion of oxide present. The degree to which this is true may be judged from the fact that in experiments where the conditions were identical except that in one there was present nitric acid and in the other it was absent decolorization was observed in the acid solution in about an hour. The neutral solution required 35 hours. In alkaline solutions the reaction is still more retarded.(2)

A solution in which the ratio of permanganate to manganese dioxide was 1:1 became decolorized in 2 hours; where the ratio was 1:7, the time required was 5 min.

The oxide precipitated from potassium permanganate or from permanganic acid is not stable in the absence of an excess of potassium permanganate and loses oxygen at a rate depending upon the temperature and humidity, but all the oxides regain the lost oxygen in the presence of even dilute permanganate, so that the ratio of manganese

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(1) Am. Chem. Jour., vol. XVIII.
(2) Dissertation, Johns Hopkins, p.20.

to oxygen in the oxide precipitated by manganese sulphate from potassium permanganate is two to one.

This fact is shown by a large number of experiments embodied in Walker's Dissertation.(1)

The observation had been made that the rate of evolution of oxygen depended also on the kind of acid present and it was this fact which led to the present investigation.

Many wholly unsuspected facts have come to light during the course of the work, some of which have been investigated while others have been left for future work.

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(1) Johns Hopkins, 94.

Description of Apparatus.

In the first experiments an attempt was made to use a large bath for the purpose of securing uniformity of temperature. It was furnished with an overflow pipe and kept constantly full from the city water supply. In this bath large glass tubes, previously filled with the solution to be tested, were immersed. These were connected with graduated tubes which were filled with water and inverted in the bath. As the oxygen was evolved it was collected in this manner and measured. After some time the contents of the tubes were analyzed.

It was found, however, that the oxide settled at the bottom of the tubes and its contact with the permanganic acid was thus made slight and not uniform. The temperature also varied to a great extent and it was found impossible to secure comparable results by these means.

Two large water-baths were then prepared. They were made of sheet-iron and covered with asbestos board. The regulation of the temperature was secured by means of

Reichardt regulators and throughout the experiments was held as close as possible to 30°C. Uniformity of temperature in all parts of the bath was obtained by means of stirrers kept in motion by a small electric motor.

The solutions subjected to examination were placed in Drechsel gas-washing cylinders. These cylinders were run in sets of four and were immersed to a point above the level of the solutions within them.

The solutions were kept constantly agitated by a current of purified air drawn through them by means of a filter pump. Changes of pressure in the water supply, which otherwise would have caused the solutions to pass back from one cylinder to the next, were rendered harmless by means of Bunsen valves interposed between the filter pump and the series of cylinders.

The air was purified by passing through a cylinder containing a concentrated solution of permanganate before entering the test solutions; it was also thus brought to the same temperature as the bath. The rapidity of the air-current and, in consequence, the amount of agitation, varied somewhat but was never so rapid but that the succession of bubbles was distinct.

The efficiency of the gas regulators was increased by allowing the gas to pass over calcium chloride and caustic potash, the fouling of the mercury being thus avoided.

The burettes and other measuring apparatus used throughout the work were calibrated by the method of Morse and Blalock,(1) so that measurments could be made which were accurate to one-hundredth of a cubic centimeter.

The water used in all the work was neutral to litmus and free from reducing substances, being prepared by the method described in Chambers's Dissertation,(2) and also in the American Chemical Journal.(3)

The Potassium permanganate solutions were prepared from the commercial salt and carefully freed from the oxide by repeated filtration through filters of ignited and washed asbestos. They were protected from dust and direct sunlight. They were standardized by means of potassium tetroxalate and the results confirmed by several other methods.

The tetroxalate was prepared in the ordinary manner

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(1) Am. Chem. Jour. 16, 479.
(2) Johns Hopkins, 96.
(3) Am. Chem. Jour., vol. 19, p.90.

and carefully purified by several recrystalizations. The acid solutions used were standardized by the usual methods. The preparation of the other solutions used will be described as they are taken up in the discussion.

Experiment I.

This experiment was designed to show the relative efficiency of sulphuric and nitric acids in hastening the reaction between manganese dioxide and permanganic acid.

The oxide was produced by means of potassium permanganate and manganese sulphate. The reaction takes place according to the equation:

$$2K\,MnO_4 + 3Mn\,SO_4 + 2H_2O = K_2SO_4 + 2H_2SO_4 + 5MnO_2.$$

It will thus be seen that for every molecule of permanganate reduced, two and a half molecules of manganese dioxide are produced and, while the potassium of the permanganate is neutralized, twice ~~an~~ the equivalent amount of acid is liberated.

The solution of permanganate used in this experement contained 41.81 m.g. of permanganate per cubic centimeter. A nearly equivalent solution of ~~M~~manganese sulphate was prepared and its relation to the permanganate accurately established by the Volhard's method.

To secure comparable conditions the following proportions were used. A fixed amount of permanganate being taken sufficient manganese sulphate was added to render the

relation of permanganate molecules to the molecules of oxide formed as two to one. The amount of acid was sufficient to neutralize three times the potassium of the permanganate unreduced while that liberated by the precipitation of the oxide was neutralized. Of course in this case the amount of acid added in the form of the manganous sulphate was considered.

The acids used were about normal solutions and since, as will be seen, the conditions of precipitation are very important, they were added to the permanganate before the precipitation was effected..

The actual procedure was:

Thirty-six cubic centimeters of $K.MnO_4$ were measured into a Drechsel cylinder; acid in sufficient quantity added and then manganese sulphate sufficient to cause the precipitation of six c.c. of the $K\ MnO_4$.

The precipitation took place at once. Then water sufficient to dilute to 90c.c. was added in order that comparable conditions as to concentration might be secured. In every series four cylinders were used, two containing sulphuric acid and two nitric acid. The air used in agitation was passed through them in every case in the order indicated

by their numbers.

An example will suffice to make the operation clear.

No. 1 and 2.	K MnO_4	36.c.c.	41.81 m.g.p c.c.
	H_2SO_4	21.76 c.c.	46.42 m.g.p c.c.
	$MnSO_4$	5.27 c.c.	= 6 e.e.$KMnO_4$
	H_2O	26.97 c.c.	
	Total	90.00 c.c.	

No. 3 and 4.	K MnO_4	36.c.c.	41.81 m.g.p c.c.
	H NO_3	20.33 c.c.	63.90 m.g.p c.c.
	$MnSO_4$	5.27 c.c.	6.c.c. K MnO_4
	H_2O	28.36 c.c.	
	Total	90.00 c.c.	

The conditions were thus as nearly identical as possible and were: Two molecules of H MnO_4 to one of MnO_2 to 3 molecules of acid. The duration of the experiments was varied slightly but they were for the most part, allowed to remain in the bath seventy hours, after which time the analysis was conducted as follows:

The cylinders were examined in the same order in which they were filled. The solution was poured into a beaker and an amount of oxalic acid exactly equivalent to the total permanganate used was measured into the cylinder.

a little sulphuric acid added and agitated until the film of oxide which had formed on the glass was removed. The whole was then added to the beaker and the cylinder carefully and repeatedly rinsed. The beaker was warmed slightly and when solution was complete the excess of oxalic acid was determined by titration with the original permanganate. It will be seen that the amount of permanganate needed to restore color is an exact measure of the oxygen evolved in accordance with the equation given by Morse and Hopkins,(1) and the number of c.c. required is equivalent to three-fifths of the number reduced to MnO_2 in the above-mentioned reaction. The results will be expressed then in amount of oxygen evolved as thus determined and in percentage reduction to MnO_2. An example will suffice to show how these data are derived from titration results.

No. 1. of series I. (see table, p.15) required 1.58 c.c $KMnO_4$ to restore color. 1 c.c. of $KMnO_4$ reduced to the manganous condition will evolve 7.40 c.c. oxygen. The amount of oxygen is therefore $1.58 \times 7.40 = 11.69$ c.c.

1 c.c. $KMnO_4$ reduced to the manganous condition is

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(1) See Introduction.

equal to 5/3 c.c. reduced to MnO_2 and there were 5/3 X 1.58 or 2.63 c.c. so reduced out of a possible thirty c.c. Therefore the percentage of reduction is

$$\frac{2.63}{30.00} = 8.76\ 0/0$$

The results can only be clearly expressed in the form of a table.

Table I.

Precipitant employed	$Mn\ SO_4$
Permanganate unprecipitated	1254.30 m.g.
Volume of solution	90.00 c.c.
Molecular ratio of $H\ MnO_4$ to MnO_2	2:1
Acids	($H_2\ SO_4$) ($H\ NO_3$)

No.	Acid	Vol.of O_2 in c.c.	Per ct.of Reduction	Mean	Ratio
Series I.		Time 65 hours.			
1.	H_2SO_4	11.69	8.76	8.72	
2.	H_2SO_4	11.54	8.67		
3.	$H\ NO_3$	19.61	14.73		
4.	$H\ NO_3$	20.42	15.33		1:172
Series II.		Time 65 hours.			
1.	$H_2\ SO_4$	10.88	8.10		
2.	$H_2\ SO_4$	10.16	7.77	7.94	
3.	$H\ NO_3$	18.29	13.73		
4.	$H\ NO_3$	20.20	15.16	14.45	1:182
Series III.		Time 65 hours.			
1.	$H_2\ SO_4$	10.73	8.07		
2.	$H_2\ SO_4$	11.25	8.43	8.25	
3.	$H\ NO_3$	20.42	15.33		
4.	$H\ NO_3$	19.24	14.43	14.88	1:1.80

Series IV. Time 70 hours.

1.	H_2SO_4	11.11	8.40		
2.	H_2SO_4	11.41	8.60	8.50	
3.	HNO_3	19.95	15.07		
4.	HNO_3	19.75	14.90	14.99	1:1.76

Series IV. Time 92 hours.

1.	H_2SO_4	16.21	12.17		
2.	H_2SO_4	16.65	12.50	12.34	
3.	HNO_3	29.75	22.33		
4.	HNO_3	29.67	22.26	22.30	1:1.80.
				Mean ratio	1:1.78.

The differences in the volumes of oxygen evolved in duplicate cylinders is not excessive and are probably due to unavoidable differences in the conditions of experiment It has been already noted that the passage of the air current was in no wise constant, being subject to the water pressure in the city mains.

The conditions of precipitation also affect the results, but it is not clear what are the best and most uniform conditions. The temperature also was somewhat variable.

The fact that the nitric acid effects a very considerably increased decomposition is not to be doubted.

Experiment II.

During the progress of the work it was noted that when the manganese sulphate was added to the permanganate previous to the addition of acid abnormal results were obtained, and it seemed of interest to determine the nature and extent of this difference.

For this purpose four cylinders were again run in series, In one pair the conditions were identical with those of the last experiment where sulphuric acid was used. and in the other pair the conditions were also the same with the exception that the acid was added after the precipitation of the oxide. Since the precipitate formed almost immediately there was but a very short interval between the addition of the $MnSO_4$ and the acid. Having made two series of observations with sulphuric acid a corresponding experiment was made using nitric acid.

The results are embodied in the Table in two parts - A. and B.

Precipitant employed	$Mn\ SO_4$
Permanganate unprecipitated	1254.3 m.g.
Volume of solution	90.0 c.c.
Molecular ratios of $H\ MnO_4$ to MnO_2	2:1
Acid used in A.	H_2SO_4
Acid used in B.	$H\ NO_3$

A. Series I. Time 70 hours.

No.	Condition of precipitation	Vol.of O in c.c.	Per ct.of Reduction	Mean	Ratio
1.	acid	10.10	7.60		
2.	acid	10.25	7.70	7.65	
3.	neutral	19.18	14.44		
4.	neutral	18.74	14.12	14.28	1:1.86.

Series II. Time 70 hours.

1.	acid	10.76	8.10		
2.	acid	10.47	7.87	7.99.	
3.	neutral	19.76	14.84	14.56	
4.	neutral	18.96	14.28	14.56	1:1.82
				Mean	1:1.84

B. Series I. Time 70 hours.

1.	acid	20.64	15.53		
2.	acid	21.45	16.13	15.83	
3.	neutral	32.11	24.06		
4.	neutral	31.26	23.54	23.80	1:1.50

Series II. Time 70 hours.

1.	acid	22.03	16.50		
2.	acid	21.59	16.26	16.38	
3.	neutral	32.10	23.06		
4.	neutral	33.31	25.06	24.56	1:1.50
				Mean	1:1.50

Experiment III.

By a consideration of the reaction between manganous sulphate and potassium permanganate it will be seen that pure conditions were not obtainable since some sulphuric acid is liberated in the formation of the oxide and is con-

sequently present in the solutions which are acidified with nitric acid. To remove this objectionable feature it was decided to prepare the oxide by means of potassium permanganate and oxalic acid.

The oxalic acid used was prepared by dissolving the commercial acid in alcohol and ether and recrystalizing several times from pure water. The reaction which takes place between oxalic acid and potassium permanganate when the latter is in excess, is represented by the following equation:-

$$2\,KMnO_4 + 3\,H_2C_2O_4 = 6\,CO_2 + 3H_2O + K_2O + 2\,MnO_2.$$

For every molecule of permanganate reduced a molecule of manganese dioxide is formed and no acid is liberated, so that the previous objection is removed and pure conditions are obtained.

If therefore to 45 c.c. of permanganate be added sufficient oxalic acid to reduce 15 c.c. to MnO_2, the ratio of molecules of permanganate to oxide is as 2:1.

Since, in the presence of some mineral acid and in the absence of excess of permanganate the reaction becomes

$$2KMnO_4 + 5H_2C_2O_4 + 3H\ SO = K_2SO_4 + 2MnSO_4 + 10\ CO_2 + 8H_2O,$$

It is only necessary to determine the amount of oxalic

required to reduce completely 9c.c of permanganate and to use that quantity for precipitation. The oxalic acid solution used was about equivalent to the permanganate solution. The amount of oxides used was again that sufficient to neutralize the alkali liberated by precipitation, and equivalent to three times the potassium of the permanganate unreduced.

The volume of the solution was 90 c.c. when placed in the bath, so that the final concentration was the same as in the previous experiments.

The object of the experiment being to determine the relative efficiency of sulphuric and nitric acids in promoting the activity of this oxide the results are given in the table.

Precipitant employed	$H_2C_2O_4$
Permanganate unprecipitated	1254.3 m.g.
Volume of the solution	90.0 c.c.
Molecular ratio of $HMnO_4$ to MnO_2	2:1.
Acids	(H_2SO_4) ( ) (HNO_3) ( )

Series I. Time 70 hours.

No.	Acid	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio.
1.	H_2SO_4	10.54	7.93		
2.	H_2SO_4	10.03	17.54	7.74	
3.	H, NO_3	65.59	49.35		
4.	$H\ NO_3$	62.98	47.34	48.35	1:6.25

Series II. Time 70 hours

1..	H_2SO_4	9.88	7.44		
2.	H_2SO_4	9.80	7.37	7.41	
3.	$H\ NO_3$	59.73	44.96		
4.	$H\ NO_3$	64.71	48.69	46.83	1.6.33

Series III. Time 70 hours

1.	H_2SO_4	10.03	7.54		
2.	...	- - - -	- - - -	7.54	
3.	$H\ NO_3$	61.71	46.45		1:6.16
4.	- - - -	- - - - -	- - - - -	46.45	

Series IV. Time 70 hours.

1.	H_2SO_4	11.05	8.33		
2.	H_2SO_4	12.09	9.09	8.71	
3.	$H\ NO_3$	73.05	54.97		
4.	$H\ NO_3$	72.32	54.44	54.71	1:6.28

Series V. Time 70 hours.

1.	H_2SO_4	11.63	8.71		
2.	H_2SO_4	11.26	8.42	8.57	
3.	$H\ NO_3$	71.69	53.77		
4.	$H\ NO_3$	72.94	54.87	54.32	1.6.22

Series VI. Time 70 hours

1..	H_2SO_4	10.89	8.18		
2.	H_2SO_4	10.97	8.22	8.20	
3.	$H\ NO_3$	68.01	51.03		
4.	$H\ NO_3$	68.89	51.69	51.36	1:6.25
				Mean	1:6.25

The remarkable behavior of the acids in this case gives reason to hope that a method may be derived from it for the determination of the quantities of free acids present in a solution containing the salts of one acid to which the other acid has been added.

This subject is at present being investigated in this laboratory.

Experiment IV.

To determine if the oxides formed by precipitation with oxalic acid in neutral solution behaved in any way similar to that from manganese sulphate. The experiment was conducted as follows:

Preliminary experiments were made to determine the time required for the formation of the oxide and it was noted that the temperature of the room and of the solutions not only affected the rapidity of the formation of the oxide but also its nature, as shown by the oxygen evolved. What the exact nature of this effect is has not been carefully investigated.

It was found that about twenty minutes were required for the formation of the oxide in the neutral solution, when, after the addition of the oxalic acid, the cylinders were placed in the bath, and a current of air conducted through them in the usual manner. The acid in requisite quantity was then added, and the duplicate pair in which the oxide had been precipitated in an acidified permanganate was placed in the bath with them.

The results of this treatment are shown below in Series I. and II.

To determine if the maximum effect of this treatment had been obtained, two more series were carried through in which the solution of permanganate used was warmed to the temperature of the bath (30°) and, the oxalic acid being introduced, were allowed to run for one hour before the acid was added.

The results of this are given in series III. and IV.

It being so shown that but little difference could be observed, the series in which nitric acid was used were warmed to 30°, the precipitation effected in half an hour, and acidified.

The results in the case of nitric acid were surpris-

ing and not in accordance with results in other experiments when different precipitants were used.

Precipitant employed	$C_2H_2O_4$
Permanganate unprecipitated	1246.5 m.g.
Volume of the solution	90.0 c.c.
Molecular ratio of $H\,MnO_4$ to MnO_2	2:1.
Acid used in A.	H_2SO_4
Acid used in B.	$H\,NO_3$

A. Series I. Time 76 hours.

No.	Condition	Vol. of O_2 in c.c.	Per ct. of reduction	Mean	Ratio.
1.	Acid	10.01	7.57		
2.	acid	9.50	7.17	7.37	
3.	neutral	11.85	8.93		
4.	neutral	11.04	8.33	8.68	1:1.17

Series II. Time 70 hours.

No.	Condition	Vol. of O_2 in c.c.	Per ct. of reduction	Mean	Ratio.
1.	acid	11.62	8.77		
2.	acid	11.26	8.56	8.64	
3.	neutral	14.28	10.77		
4.	neutral	14.72	11.10	10.94	1:1.26

Series III. Time 74 hours.

No.	Condition	Vol. of O_2 in c.c.	Per ct. of reduction	Mean	Ratio.
1.	acid	12.51	9.43		
2.	acid	12.22	9.23	9.33	
3.	neutral	15.46	11.67		
4.	neutral	15.68	11.83	11.75	1:1.26

Series IV. Time 71 hours.

1.	acid	12.14	9.17		
2.	acid	11.78	8.90	9.04	
3.	neutral	14.87	11.23		
4.	neutral	14.13	10.67	10.95	1:1.21
				Mean ratio	1:1.23

B. Series I. 68 hours.

1.	acid	65.21	49.23		
2.	acid	65.95	49.77	49.50	
3.	neutral	48.58	36.67		
4.	neutral	50.64	38.23	37.95	1:0.77

Series II. Time 68 hours.

1.	acid	67.94	51.27		
2.	acid	66.98	50.57	50.92	
3.	neutral	50.42	38.07		
4.	neutral	50.56	38.17	38.12	1:0.75
				Mean ratio	1:0.76

Experiment V.

Since the amount of oxygen evolved varies somewhat in the different series though the ratio remains quite constant, it seemed desirable to compare the oxides from manganese sulphate directly with that from oxalic acid rather than depend upon the comparison obtainable from the preceeding experiments. When 36 c.c. of permanganate

are treated with sufficient manganese sulphate to reduce 6 c.c. to the form of the oxide, the relation of permanganate to manganese dioxide is the same as when 45 c.c. of the same permanganate are treated with sufficient oxalic acid to precipitate 15 c.c. The amount of acids being so determined that the final acidity should be identical in both cases. The experiment was carried out in two parts:

A, where sulphuric acid is used

B, where nitric acid is used.

In each case the ratio of $H MnO_4$ to MnO_2 to acid being as 2:1:3.

Precipitants employed	($MnSO_4$) ($H_2C_2O_4$)
Permanganate unprecipitated	1246.5 m.g.
Volume of solution	90.0c.c.
Molecular ratio of $H MnO_4$ to MnO_2	2:1.
Acid used in A.	H_2SO_4
Acid used in B.	$H NO_3$

A. Series I. Time 70 hours.

No.	Precipitant	Vol.of O in c.c.	Per ct.of decomposition.	Mean	Ratio
1.	$MnSO_4$	12.22	9.23		
2.	$MnSO_4$	11.92	9.00	9.12	
3.	$H_2C_2O_4$	10.97	8.27		
4.	$H_2C_2O_4$	10.67	8.07	8.17	1.0.90

Series II. Time 70 hours.

1.	$MnSO_4$	12.58	9.50		
2.	$MnSO_4$	13.54	10.23	9.87	
3.	$H_2C_2O_4$	11.04	8.33		
4.	$H_2C_2O_4$	11.19	8.43	8.38	1:0.85

Series III. Time 70 hours.

1.	$MnSO_4$	12.58	9.50		
2.	$MnSO_4$	13.54	10.23	9.87	
3.	$H_2C_2O_4$	11.04	8.33		
4.	$H_2C_2O_4$	11.19	8.43	8.38	1:085

Series IV. Time 70 hours.

1.	$MnSO_4$	12.36	9.33		
2.	$MnSO_4$	13.03	9.83	9.58	
3.	$H_2C_2O_4$	11.41	8.60		
4.	$H_2C_2O_4$	10.45	7.90	8.25	1:0.86
				Mean	1:0.87

B. Series I. Time 70 hours.

1.	$MnSO_4$	20.65	15.50		
2.	$MnSO_4$	20.49	15.40	15.45	
3.	$H_2C_2O_4$	64.97	48.77		
4.	$H_2C_2O_4$	64.97	48.77	48.77	1:3.16

Series II. Time 70 hours.

1.	$MnSO_4$	24.23	18.02		
2.	$MnSO_4$	24.74	18.61	18.32	
3.	$H_2C_2O_4$	71.44	53.78		
4.	$H_2C_2O_4$	71.59	53.88	53.83	1:2.94

Series III. Time 70

1.	......	.....	.....	.....	
2.	$MnSO_4$	22.55	16.95	16.95	
3.	$H_2C_2O_4$	71.88	53.48		
4.	$H_2C_2O_4$	70.05	52.73	53.11	1:3.15

Series IV. Time 70 hours.

1.	$Mn SO_4$	21.67	16.36		
2.	$Mn SO_4$	21.81	16.43	16.37	
3.	$H_2C_2O_4$	66.69	50.18		
4.	$H_2C_2O_4$	67.49	50.48	50.33	1:3.08

Series V. Time 70 hours

1.	$Mn SO_4$	21.45	16.13		
2.	$Mn SO_4$	22.11	16.63	16.38	
3.	$H_2C_2O_4$	67.12	50.51		
4.	$H_2C_2O_4$	69.96	52.63	51.71	1:3.14

Series VI. Time 70 hours.

1.	$Mn. SO_4$	21.74	16.36		
2.	$Mn SO_4$	21.45	16.13	16.25	
3.	$H_2C_2O_4$	65.95	49.62		
4.	$H_2C_2O_4$	65.22	49.09	4 .36	1:3.03

Mean Ratio 1:3.08

Experiment VI.

Sugar is decomposed by permanganic acid, the products being carbon-dioxide and water. If the permanganic acid is in excess it is reduced to MnO_2. This reaction takes place slowly, and it is not practicable to determine the reducing-power of a solution of sugar by direct titration. Therefore a good specimen of rock-candy was procured. A weighed portion (8.4907 g.) was dissolved in a liter of water, and its relation to the permanganate solution determined according to the following equation:

$$C_{12}H_{22}O_{11} + 16\,KMnO = 16\,MnO_2 + 8K_2O + 12\,CO_2 + 11\,H_2O.$$

The oxide so formed differed greatly in appearance from that produced by oxalic acid and manganese sulphate. The latter being voluminous and reddish-brown in color while that from sugar was black and hard, adhering in scales to the sides of the cylinders. The experiment is designed to show the relative effects of sulphuric and nitric acid upon the activity of this oxide.

For this purpose the conditions were made identical with those of experiment.III., except that the precipitant employed was sugar. The results follow:

Precipitant employed	$C_{12}H_{22}O_{11}$.
Permanganate unprecipitated	1246.5 m.g.
Volume of the solution	90.0 c.c.
Molecular rates of $HMnO_4$ to MnO_2	2:1.
Acids employed -----------	H_2SO_4 HNO_3

Series I. Time 72 hours.

No.	Acid	vol.of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	H_2SO_4	14.50	10.93		
2.	H_2SO_4	12.07	9.10	10.02	
3.	HNO_3	25.31	19.10		1:2.00
4.	HNO_3	26.20	20.90	20.00	
Series II.	Time 70 hours.				
1.	H_2SO_4	14.27	10.81		
2.	H_2SO_4	14.90	11.29	11.05	
3.	HNO_3	28.05	21.27		
4.	HNO_3	27.84	20.95	21.11	1:1.91
Series III.	Time 71 hours.				
1.	H_2SO_4	13.08	9.92		
2.	H_2SO_4	13.00	9.85	9.89	
3.	HNO_3	28.54	21.66		
4.	HNO_3	29.88	22.65	22.16	1:2.24

Mean 1:2.05

Experiment VII.

In order to compare the oxide from sugar directly with that from manganese sulphate, it is necessary to know when the oxide from the sugar is completely formed, and since during its formation some oxygen would be given off, due to the reaction between the oxide formed and the permanganate, it was impossible by any simple means to determine the exact time of the disappearance of the sugar. The preliminary experiments showed that in about 18 hours the the loss of oxygen was equivalent to the theoretical amount due to the oxidation of the sugar.

This then was taken as the standard and the sugar solutions being prepared as in the preceding experiment were allowed to run 18 hours in the bath, after which time the manganese sulphate cylinders with which they were to be compared were placed in the bath.

No attempt was made to determine the time in which the oxidation of the sugar took place in nitric acid.

In order to lessen the percentage of error arising from the uncertain factors in this experiment, the time was extended so that the manganese sulphate cylinders ran 144 hours. It will be seen that the results of an experiment

of this kind can only be approximate. The results are here tabulated:

Precipitants employed	$C_{12}H_{22}O_{11}$: $MnSO_4$
Permanganate unprecipitated	1246.5 m.g.
Volume of solutions	90.0c.c.
Molecular ratio of $HMnO_4$ to MnO_2	2:1.
Acid used in A.	H_2SO_4
Acid used in B.	HNO_3

A. Series I.

No.	Time	Precip-tant	vol.of O in c.c.	Per. ct.of reduction	Mean	Ratio
1.	144	$MnSO_4$	25.91	19.53		
2.	144.	$MnSO_4$	26.72	20.17	19.85	
3.	164	$C_{12}H_{22}O_{11}$	25.98	18.90		
4.	164	$C_{12}H_{22}O_{11}$	25.12	19.60	19.25	1:0.97

Series II.

No.	Time	Precip-tant	vol.of O in c.c.	Per. ct.of reduction	Mean	Ratio
1.	144	$MnSO_4$	29.39	21.17		
2.	144	$MnSO_4$	29.01	21.93	22.05	
3.	163	$C_{12}H_{22}O_{11}$	28.41	20.33		
4.	163	$C_{12}H_{22}O_{11}$	28.56	20.43	20.38	1:0.90

Series III.

No.	Time	Precip-tant	vol.of O in c.c.	Per. ct.of reduction	Mean	Ratio
1.	145	$MnSO_4$	27.16	21.43		
2.	145	$MnSO_4$	28.41	20.50	20.97	
3.	163	$C_{12}H_{22}O_{11}$	32.38	24.67		
4.	163	$C_{12}H_{22}O_{11}$	32.75	24.93	24.80	1:1.18

Mean Ratio 1.02

B. Series I.

1.	142 1/2	$MnSO_4$	47.84	36.10		
2.	142 1/2	$MnSO_4$	47.99	36.23	36.17	
3.	161	$C_{12}H_{22}O_{11}$	57.85	43.67		
4.	161	$C_{12}H_{22}O_{11}$	59.69	45.07	44.32	1:1.23

Series II.

1.	142	$MnSO_4$	50.93	38.43		
2.	142	$MnSO_4$	50.85	38.40	38.42	
3.	161	$C_{12}H_{22}O_{11}$	61.82	46.67		
4.	161	$C_{12}H_{22}O_{11}$	61.47	46.43	46.55	1:1.21

Mean ratio 1:1.22

Experiment VIII.

The oxides produced by the different reducing agents previously used are of such varying efficiency that it seemed desirable to produce oxides by other methods also.

Sodium sulphite with an excess of permanganate is oxidized according to the following reaction:

$$2K\,MnO_4 + 3Na_2SO_3 = 3Na_2SO_4 + 2\,MnO_2 - K_2O.$$

That sodium sulphite could be titrated with permanganate was shown as follows: The sodium sulphite solution which was nearly equivalent to the permanganate, was dropped from a burette into the neutral permanganate, and the loss of oxygen determined by titration with oxalic acid and permanganate. It was found that precipitation was

very rapid and accorded very closely with the theoretical reduction. The strength of the sulphite solution thus determined was slightly different from that determined by the well known iodine method, but not more than is to be expected in dealing with such concentrated solutions.

That comparatively constant titrations could be obtained is shown by a series of six titrations made in rapid succession as follows:

twenty-one c.c. permanganate were measured into each of six beakers and exactly ten c.c. of sodium sulphite added, after standing five minutes oxalic acid equivalent to the total permanganate was added, together with an excess of sulphuric acid and the reduction determined by the original permanganate:

No. 1.	8.11	No. 4.	8.16		
No. 2.	8.11	No. 5	8.13		
No. 3.	8.15	No. 6	8.13	Mean	8.132

This was considered as sufficiently accurate for our purpose, and a comparison of the effects of nitric and sulphuric acids on this oxide was undertaken.

The sulphite used was the commercial product and contained some carbonate, as was shown by a small quantity of gas which was liberated when the acid was introduced. This

gas was shown to be carbon-dioxide, but the quantity was small and the amount of acid neutralized by its liberation was not considered, and would be in any case of equal amount in the solutions compared. This solution is of course quite unstable and its reducing power was determined for each series of experiments. The conditions of the experiment were as in the former cases.

The oxide was precipitated in neutral solution, and the requisite amounts of acid added after the sulphite had been oxidized. The results follow:

Precipitant employed	Na_2SO_3
Volume of the solution	90.c.c.
Permanganate unprecipitated	1246.5 m.g.
Molecular ratio of $HMnO_4$ to MnO_2	2:1.
Acids used	: HNO_3 : : : : H_2SO_4 :

Series I. Time 70 hours.

No.	acid	vol.of O.	Per ct.of reduction.	Mean	Ratio
1.	H_2SO_4	10.12	7.68		
2.	H_2SO_4	10.26	7.76	7.72	
3.	HNO_3	14.76	11.19		
4.	HNO_3	14.83	11.26	11.23	1:1.44

Series II. Time 70 hours.

1.	H_2SO_4	10.69	8.01		
2.	H_2SO_4	10.90	8.22	8.12	
3.	HNO_3	17.79	13.50		
4.	HNO_3	17.99	13.66	13.58	1:1.67

Series III. Time 70 hours

1.	H_2SO_4	10.69	8.01		
2.	H_2SO_4	11.11	8.41	8.21	
3.	HNO_3	16.73	12.50		
4.	HNO_3	17.43	13.21	12.86	1:1.57
				Mean	1:1.56

Experiment IX.

A number of determinations were made to find if a comparison of the acids could be made on an oxide precipitated in an acidified solution. It was found that, if the tip of the burette from which the sulphite was measured was passed through a two-holed rubber stopper which fitted the neck of the cylinder containing the permanganic acid and, after the addition of the sulphite, tightly closed with glass plugs, there was little or no loss of sulphurdioxide. The cylinder was agitated for a few moments before the glass stopper was put in place, and agitation se-

cured by the passage of the air current. The conditions were, therefore, identical with those in the previous experiment, except that the oxide was formed in acid solution:

Precipitant employed	Na_2SO_3
Permanganate unprecipitated	1246.5 m.g.
Volume of solution	90.0 c.c.
Ratio of $H MnO_4$ to MnO_2	2:1.
Acids used	: H_2SO_4 : : : : $H NO_3$:

Series I. Time 70.5 hours.

No.	Acids	Vol.of O. in c.c.	Per ct.of reduction	Mean	Ratio
1.	H_2SO_4	26.17	19.75		
2.	H_2SO_4	23.56	17.78	18.77	
3.	$H NO_3$	29.72	22.40		
4.	$H NO_3$	30.02	22.64	22.52	1:1.20
	Series II. Time 70 hours.				
1.	H_2SO_4	22.84	16.97		
2.	H_2SO_4	23.57	17.88	17.43	
3.	$H NO_3$	29.36	22.14		
4.	$H NO_3$	31.61	23.82	22.98	1:1.82
	Series III. Time 70 hours.				
1.	H_2SO_4				
2.	H_2SO_4	24.72	18.63	18.63	
3.	$H NO_3$	30.45	22.96		
4.	$H NO_3$	29.50	22.24	22.60	1:1.21

Mean 1:1.24

Experiment X.

In order that a direct comparison might be made between the oxides produced by the use of oxalic acid and the sodium sulphite two series of determinations were carried through.

A. The oxides from both were formed in neutral permanganate and subsequently acidified with sulphuric acid. The oxide from the oxalic acid being allowed half an hour for its formation.

B. The oxides produced in acidified permanganate in both cases and the acid employed being H_2SO_4 .

Precipitants employed	: $H_2C_2O_4$: : : : Na_2SO_3 :
Permanganate unprecipitated	1246.5 m.g.
Volume of solution	90.c.c.
Molecular ratio of $H\,MnO_4$ to MnO_2	2:1
Acid used in A.	H_2SO_4
Acid used in B.	H_2SO_4 .

A. Series I. Time 72 hours.

No.	Precipitant.	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	$H_2C_2O_4$	14.13	10.72		
2.	$H_2C_2O_4$	14.27	10.81	10.77	
3.	Na_2SO_3	11.67	8.83		
4.	Na_2SO_3	12.44	9.44	9.14	1:0.85

Series II. Time 70 hours.

No.	Precipitant.	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	$H_2C_2O_4$	13.78	10.46		
2.	$H_2C_2O_4$	14.34	10.88	10.67	
3.	Na_2SO_3	12.58	9.53		
4.	Na_2SO_3	11.95	9.05	9.29	1:0.87

Mean 1:0.86

B. Series I. Time 70 hours.

No.	Precipitant.	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	$C_2H_2O_4$	10.87	8.20		
2.	$C_2H_2O_4$	10.73	8.10	8.15	
3.	Na_2SO	27.92	21.06		
4.	Na_2SO_3	29.14	21.32	21.19	1:2.60

Series II. Time 70 hours.

No.	Precipitant.	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	$C_2H_2O_4$	11.24	8.46		
2.	$C_2H_2O_4$	11.24	8.45	8.46	
3.	Na_2SO_3	28.71	21.65		
4.	Na_2SO	28.64	21.60	21.63	1:2.56

Series III. Time 70 hours.

No.	Precipitant.	Vol. of O. in c.c.	Per ct. of reduction	Mean	Ratio
1.	$C_2H_2O_4$	11.45	8.63	8.92	
2.	$C_2H_2O_4$	12.28	9.20		
3.	Na_2SO_3	27.19	20.50	21.47	1:2.41
4.	Na_2SO_3	29.65	22.37		

Mean 1:2.52

Experiment XI.

When an excess of $KMnO_4$ is added to a solution of Potassium nitrite, reaction takes place according to the equation,

$$2KMnO_4 + 3KNO_2 = K_2O + 3KNO_3 + 2MnO_2 .$$

To determine the reducing power of the nitrite solutions, use was made of the same method as in the case of the sulphite. The purpose of this experiment is to determine the relative activity of the oxide produced by the above reaction and that produced by oxalic acid in a similar manner. Both oxides were formed in neutral solution and acidified after the precipitation of the oxide was complete.

The commercial nitrite was used and, since this contains free alkali, the amount was determined and acid sufficient to neutralize it was added in addition to that required by the conditions of the experiment.

The procedure was the same as in the experiment with sodium sulphite (see p.36.) The results are given in the table:

Precipitants used	:$C_2H_2O_4$: : : :$K\ NO_2$:
Permanganate unprecipitated	1246.5 m.g.
Volume of the solution	90.0 c.c.
Ratio of $H\ MnO_4$ to MnO_2	2:1.
Acid used in <u>A</u>.	H_2SO_4
Acid used in <u>B</u>.	$H\ NO_3$

A. Series I. Time 70 hours.

No.	Precipitant	Vol.of O. in c.c.	Per ct.of reduction	Mean	Ratio
1.	$C_2H_2O_4$	14.21	10.73		
2.	$C_2H_2O_4$	14.28	10.76	10.75	
3.	$K\ NO_2$	42.41	31.99		
4.	$K\ NO_2$	42.70	32.22	32.11	1:2.99

Series II. Time 70 hours.

No.	Precipitant	Vol.of O. in c.c.	Per ct.of reduction	Mean	Ratio
1.	$C_2H_2O_4$	15.01	11.32		
2.	$C_2H_2O_4$	14.86	11.22	11.27	
3.	$K\ NO_2$	41.76	31.49		
4.	$K\ NO_2$	42.78	32.25	31.87	1:2.82
				Mean	1:2.91

B. Series I. Time 70 hours.

No.	Precipitant	Vol.of O. in c.c.	Per ct.of reduction	Mean	Ratio
1.	$H_2C_2O_4$	42.78	32.25		
2.	$H_2C_2O_4$	48.36	36.48	34.37	
3.	$K\ NO_2$	73.66	55.55		
4.	$K\ NO_2$	72.65	55.12	55.34	1:1.61

Series II. Time 71 hours.

1.	$H_2C_2O_4$	48.01	36.35		
2.	$H_2C_2O_4$	47.01	35.37	35.86	
3.	KNO_2	72.07	54.33		
4.	KNO_2	72.43	54.62	54.48	1:1.52

Series III. Time 70 hours.

1.	$H_2C_2O_4$	47.01	35.37		
2.	$H_2C_2O_4$			35.37	
3.	KNO_2	71.76	54.13		
4.	KNO_2	68.73	51.84	52.99	1:1.49

Series IV. Time 70 hours.

1.	$H_2C_2O_4$	49.10	37.16		
2.	$H_2C_2O_4$	47.11	35.66	36.35	
3.	KNO_2	71.81	54.27		
4.	KNO_2	73.79	55.77	55.02	1:1.51

Series V. Time 35 hours

1.	$C_2H_2O_4$	27.61	20.10		
2.	$C_2H_2O_4$	27.73	20.87	20.48	
3.	KNO_2	40.79	30.83		
4.	KNO_2	41.75	32.67	31.75	1:1.55

Series VI. Time 35 hours.

1.	$C_2H_2O_4$	25.50	19.27		
2.	$C_2H_2O_4$	27.61	20.10	19.69	
3.	KNO_2	40.43	30.57		
4.	KNO_2	39.84	30.10	30.34	1:1.54
				Mean	1:1.54

Experiment XII.

It seemed desirable to determine the activity of the oxide formed by potassium nitrite when added to solutions already acidified with sulphuric and with nitric acids. It is obvious that the same difficulty ~~is~~ must be encountered here as in the case of the sulphite, and it was found that, if the precipitation was made in the manner indicated in experiment IX., there was but little loss of oxides of nitrogen. The oxygen of the air above the solution assisted in the oxidation of any nitrous acid which escaped into it, and as a result the true reducing power of the nitrite solution could not be obtained. The titrations showed that constancy in results could be obtained by careful work and the experiment was carried out.

Precipitant employed	KNO_2
Permanganate unprecipitated	1246.5 m.g.
Volume of the solution	90. c.c.
Molecular Ratio of $HMnO_4$ to MnO_2	2:1.
Acids used	: HSO_4 : : HNO_3 :

Series I. Time 70 hours.

No.	acid	O. evolved in c.c.	Per ct.of reduction	Mean	Ratio
1.	H_2SO_4	25.45	19.19	19.14	
2.	H_2SO_4	25.30	19.09		
3.	HNO_3	61.70	46.19		
4.	HNO_3	61.05	46.03	46.11	1:2.41

Series II. Time 70 hours.

1.	H_2SO_4	29.22	22.05		
2.	H_2SO_4	33.05	23.06	22.56	
3.	HNO_3	60.97	46.03		
4.	HNO_3	65.66	49.54	47.79	1:2.12

Series III. Time 70 hours

1.	H_2SO_4	29.44	22.17		
2.	H_2SO_4	27.93	22.41	22.29	
3.	HNO_3	64.53	48.65		
4.	HNO_3	63.51	47.96	18.31	1:2.17
				Mean	1:2.23

Experiment XIII.

That no very rapid evolution of oxygen takes place as a result of the decomposition of neutral permanganate by MnO_2 produced by means of manganese sulphate is shown by the experiments recorded by Morse, Hopkins and Walker.(1) To make a similar determination in case of the oxides from oxalic acid, sodium sulphite and potassium nitrite was the object of the following experiment. The experiment was conducted in a like manner and under similar conditions with those previously recorded with the exception that the solutions were diluted to 90 c.c. without the addition of acid. It will be noted that, compared with the acidified solutions the evolution of oxygen is extremely small.

Precipitants used	: $H_2C_2O_4$: : N_2SO_3 : : $K NO_2$:
Permanganate unprecipitated	1245.5 m.g.
Volume of the solution	90.0 c.c.
Ratio of $K MnO_4$ to MnO_2	2:1.

No acid employed.

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A. Series I. Time 70 hours.

No.	Precip-tant.	Vol.of O. in c.c.	Per ct.of reduction.	Mean	Ratio.
1.	$H_2C_2O_4$	.91	.70		
2.	$H_2C_2O_4$	.63	.48	.59	
3.	Na_2SO_3	1.34	1.02		
4.	Na_2SO_3	1.20	.90	.96	1:1.63

Series II. Time 70 hours.

1.	H_2C_2O	1.05	.79		
2.	$H_2C_2O_4$	.96	.64	.72	
3.	Na_2SO_3	1.41	1.05		
4.	Na_2SO_3	1.27	.96	1.01	1:1.40

Series III. Time 70 hours.

1.	$H_2C_2O_4$	.63	.48		
2.	$H_2C_2O_4$	.49	.38	.43	
3.	Na_2SO_3	.98	.73		
4.	Na_2SO_3	1.27	.96	.85	1:1.98

B. Series I. Time 70 hours.

1.	$H_2C_2O_4$	1.02	0.77		
2.	$H_2C_2O_4$	.87	0.67	.72	
3.	$K NO_2$				
4.	$K NO_2$	.22	0.16	.16	1:1.22

Series II. Time 70 hours.

1.	$H_2C_2O_4$	1.09	.83		
2.	$H_2C_2O_4$	1.45	1.10	.97	
3.	K NO_2	0.00	0.0		
4.	K NO_2	0.36	0.27	.14	1:0.14
				Mean	1:0.18

General Statement.

In order to present the results of the investigation in as compact form as possible the appended table was prepared. A few words will suffice to show how it is arranged.

In the first vertical column are given the names of the substances used to precipitate the oxide from the premanganate. They are numbered for convenience of reference to other parts of the table. In column I. are given the amounts of oxygen evolved, in the different cases where the oxide was formed in the presence of sulphuric acid. This is expressed in decimal fractions of a cubic centimeter per hour, and is obtained by taking

the mean of all the observations made where that particular precipitant was used in permanganate acidified with sulphuric acid.

The number of separate estimations upon which this mean is based is placed above the volume per hour.

In column II. are arranged similar values for the cases where the oxide was formed in nitric acid solutions. In column III. are placed the corresponding values where the oxide was formed in neutral solution and then acidified with H_2SO_4 .

In column IV. the same values are given for oxide precipitated by neutral solution and acidified with nitric acid.

In column A. is given the ratio shown in the quantity of oxygen evolved when sulphuric and nitric acid are compared in regard to their effect on the oxide formed in acidified solutions. The bracketed values are those obtained by direct experiment, and those in the next lower space are obtained by comparing the values in columns I. and II.

Column B. gives corresponding values for the oxide

formed in neutral solution. Columns C., D., E., F. show the relative activities of the different oxides under the same conditions.

Columns G. and H. show the relative values for oxides produced in acid and neutral, subsequently acidified, solutions for both sulphuric and nitric acids. In addition to the table it may be remarked that while sufficient data have not been obtained to give a firm basis for a conclusion in reference to the influence of time on the rate of the reaction, yet these following facts are of interest.

The oxide formed by the use of manganese sulphate shows an increase in the rapidity of the evolution of oxygen with increasing duration of the experiment. In sulphuric acid the volume of oxygen evolved per hour is given.

6	experiments	running	65 hrs.	.1699 c.c. per hr.
12	"	"	70 "	.1660 c.c. "
2	"	"	92 "	.1785 c.c. "
6	"	"	144 "	.1928 c.c. "

In nitric acid

15	experiments	running	70 hrs.	.3130 c.c.	"
2	"	"	92 "	.3229 c.c.	"
4	"	"	144 "	.3479 c.c.	"

A reverse phenomenon appears, however, in the cases where oxides produced by other means were used.

Sugar forms in sulphuric acid solutions of permanganate an oxide which shows the following rates of evolution:

6	experiments	running	71 hrs.	.1920 c.c.	per hr.
6	"	"	164 "	.1760 c.c.	"

In nitric acid solutions:

6	experiments	running	71 hrs.	.3894 c.c.	per hrs.
4	"	"	161 "	.3739 c.c.	"

This ~~being~~ is the case, notwithstanding the fact that a considerable period of time is required for the formation of the oxide.

For the oxygen produced in nitric acid solutions by oxalic acid:

	I. H_2SO_4	II HNO_3	III ppt. Neutral. H_2SO_4	IV ppt. Neutral. HNO_3	A Ratio I:II
1. $MnSO_4$. Oxygen in c.c. per hr.	No. of exp. 26.	No. of exp. 29.	No. of Exp. 4.	No. of exp. 4	(1:1.78)
	.1740	.3175	.27 37	.4597	1:1.83
2. $C_2H_2O_4$ O_2 in c.c. per hr.	No. of exp. 32	No. of exp 29.	No. of exp. 20	No. of exp. 15	(1:6.25)
	.1567	.9633	.1988	.7109	1:6.15
3. $C_{12}H_{22}O_{11}$ O_2. in c.c. per hr.	No. of exp. 12.	No. of exp. 10.			(1:2.05)
	.1890	.3822			1:2.03
4. Na_2SO_3 O_2. in c.c. per hr.	No. of exp. 11.	No. of exp 6.	No. of exp. 14.	No. of exp. 6.	(1:1.24)
	.3791	.4301	.1677	.2370	1:1.14
5. KNO O_2. in c.c. per hr.	No. of exp. 4.	No. of exp. 4.	No. of exp. 4.	No. of exp. 12.	(1:2.23)
	.4101	.8986	.6059	1.0736	1:2.19

B Ratio III:IV.	C Ratio of 1:2,3,4,5 of I.	D Ratio of 1:2,3,4,5 of II.	E Ratio of 1:2,3,4,5 of III.	F Ratio of 1:2,3,4,5 of IV.	G Ratio of I:III.	H Ratio of II:IV.
					(1:1.84)	(1:1.50)
1:1.68	1.	1.	1.	1.	1:1.56	1:1..45
	(0.87)	(3.08)			(1:1.23)	(1:0.76)
1:3.58	0.90	3.03	.73	1.55	1:1.27	1:0.74
	(1.02)	(1.22)				
1:	1.09	1.21				
(1:1.56)	(2.19)		(0.63)			
1:1.41	2.18	1.35	.61	.52	1:0.45	1:0.55
			(2./3)	(2.39		
1:1.77	2.36	2.83	2.21	2.34	1:1.48	1:1.19

4 experiments running 35 hrs., .7745 c.c. per hr.

11 " " 70 " .6878 c.c. "

In the case of the oxide from potassium nitrite -

4 experiments running 36 hrs., 1.1629 c.c. per hr.

8 " " 70 " 1.0302 c.c. "

These phenomena deserve a closer examination as they have a bearing upon the question to be discussed in the second portion of this paper.

Conclusions.

1. There is a very decided difference in the influence of nitric acid and of sulphuric acid upon the rapidity of the reaction between permanganic acid and the oxides formed by precipitation of the permanganic acid by reducing agents. The influence of the nitric acid is by far the greater.

2. The oxides formed by the different reducing agents differ as regards this reaction though the ratio of

manganese to oxygen is as one to two in all of them.

3. The oxide, if formed in neutral permanganate and subsequently acidified, differs in efficiency from that precipitated in acidified solutions, but this difference is not always in the same direction. For the most part it is less efficient under the latter circumstances, but in the case of the oxide formed by oxalic acid with the nitric acid the reverse is true as also with that from sodium sulphite in both sulphuric and nitric acids.

4. The oxides produced by the different reagents used differ markedly in appearance. Some are hard and black, some are voluminous and of a reddish-brown color, while others are dark in color though voluminous. Sometimes the oxides formed bright iridescent films on the walls of the vessels and sometimes failed to adhere to them at all.

However, each oxide seemed to possess distinct characteristics.

5. The oxides from the different sources appear to decompose the neutral permanganate at varying rates, but the amount of evidence upon this point is not sufficient to give a basis for a conclusion.

We find considerable difficulty in assigning anything as a sufficient explanation of these phenomena. However a study of the conditions may make evident some considerations which render it probable that the differences observed are due to no single cause.

In the first place the fact that the oxides formed under the different conditions of precipitation differ from one another so markedly in appearance indicates a probable difference in molecular complexity. That these oxides are very complex and contain varying amounts of water and base has been shown by many observers. It seems reasonable to suppose therefore that the acids would affect the composition of these oxides differently, and that this difference in composition would reveal itself in different degrees of activity of the oxide formed. Moreover that the pres-

ence of the acids would liberate permanganic acid from the permanganate is scarcely to be doubted, but the extent to which this reaction would take place would depend not only on the relative avidities of the acids employed but upon the avidity of the permanganic acid itself. The liberation of an increased proportion of the less stable permanganic acid by the nitric acid would therefore cause an increase in the rate of the reaction between it and the oxide.

While it is known that neither sulphuric acid nor nitric acid in dilute solution is capable of reducing permanganic acid nor of oxidizing manganese dioxide, yet it is conceivable that the presence of the free acid ions in the solutions would lessen the stability of the permanganic acid owing to the affinity of these ions for the manganese present and this influence would be proportional to the number of ions present.

It was shown by Walker (1) that when neutral per-

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(1) Am. Chem. Jour., 18, 411.

manganate was decolorized by manganese dioxide the supernatant liquid when perfectly filtered contained no base and was without alkaline reaction or oxidizing power, that is, all the potassium is precipitated with the oxide. Now we know that when this oxide is acidified with nitric acid it becomes more active than the same oxide when acidified with sulphuric acid. It would appear that this difference should bear a direct relation to the avidities of the acids. We find however that in the case where the oxide is formed by precipitation with oxalic acid the relation thus found is 1:3.58, while, where the oxide is formed by use of potassium nitrate, the relation becomes 1:1.77. This however does not imply that the acids are dissociated to different degrees in the same solution for in no experiment except in the case of precipitation by means of oxalic acid do we have what may be called pure conditions. This will be easily seen from a consideration of the table which follows:

Under (a) is given the proportionate quantities of the compounds present in each experiment where sul-

phuric acid is used with the reducing agent indicated.

Under (b) ~~is~~ are given corresponding data where nitric acid is used. In this we assume, what cannot be strictly true, ~~namely,~~ that all the potassium present in the solutions forms neutral salts with the acids, and that there is no interchange of base where two acids or their salts are present in the same solution.

The relative influence of the acids on oxides formed in acid solution is given under each case.

Oxalic acid -

a) $2H\,MnO_4 : MnO_2 : 3/2\ K_2SO_4 : 2H_2SO_4$

b) $2H\,MnO_4 : MnO_2 : 3K\,NO_3 : 4H\,NO_3$

1:6.25

Manganese Sulphate -

a) $2H\,MnO_4 : MnO_2 : 3/2K_2SO_4 : 2H_2SO_4$

b) $2H\,MnO_4 : MnO_2 : 3K\,NO_3 : \left(\begin{array}{l} 87\%\ 4H\,NO_3 \\ \\ 13\%\ H_2SO_4 \end{array}\right)$ 1:1.78

Sodium Sulphite

a) $2H\,MnO_4 : MnO_2 : \left(\begin{array}{l} 3/2\ K_2SO_4 \\ \\ 3/2\ Na_2SO_4 \end{array}\right) : 2H_2SO_4$

b) $2H\,MnO_4 : MnO_2 : \left(\begin{array}{l} 3K\,NO_3 \\ \\ 3/2\ Na_2SO_4 \end{array}\right)\ 4H\,NO_3$

1:1.24

Potassium Nitrite

a) $2H\ MnO_4 : MnO_2 : \left(\begin{array}{c} 3/2\ K\ NO_3 \\ \\ 3/2\ K_2SO_4 \end{array}\right) : 2H_2SO_4$

b) $2H\ MnO_4 : MnO_2 : 9/2\ K\ NO_3 : 4H\ NO_3$ 1:2.23

Sugar -

a) $2H\ MnO_4 : MnO_2 : 3/2\ K_2SO_4 : 2H_2SO_4$
b) $2H\ MnO_4 : MnO_2 : 3K\ NO_3 : 4H\ NO_3$ 1:2.05

It ~~must~~ should be noted that the conditions of the experiment upon sugar were such as to preclude the placing of much reliance upon the results, since the oxide tended so strongly to harden and cling to the sides of the containing vessels that agitation with the solution could not but be decreased.

It should also be added that an experiment performed since the completion of this work indicates that a small amount of sulphuric acid in the nitric acid solutions retards the reaction to a degree dis-

proportionate with the amount present. This will be subjected to an investigation.

Moreover it was stated by Bemmelen (1) that manganese dioxide decomposes the salts of the alkalies with the liberation of acid.

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(1) Jour. für Pr. Chem. vol.131, 342.

PART II.

Introduction.

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Victor Meyer and Max von Recklinhausen[1] in 1896 published the results of some experiments on the liberation of oxygen when hydrogen and carbon-monoxide are absorbed by acidified solutions of potassium permanganate. In this article they claim that the reaction reaches a definite limit, and state that no explanation which they are able to devise is sufficient to account for this remarkable liberation of oxygen.

Morse,[2] in an article which did not reach the publishers until after the appearance of a subsequent article by Hirtz and V. Meyer, suggested that this evolution of oxygen was due to the action of the manganese dioxide formed by the reduction of the permanganic acid by the carbon monoxide and hydrogen , and is therefore the same kind of reaction as that described by himself and

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(1) Ber. d. Chem. Ges. 29; 2549.
(2) Ibid. 3048.

others at an earlier date.(1)

In the communication of Hirtz and V. Meyer(2) the similarity of the phenomena is denied chiefly on the ground of a "~~C~~crucial ~~E~~experiment" which they conducted as follows: When the hydrogen had been wholly absorbed and the oxygen removed from the tube and replaced by carbon monoxide and the agitation continued for an equal length of time, there was no appreciable increase in the volume of oxygen evolved. The question was taken up by Morse and Reese(3) with reference to the reaction when hydrogen was used. They arrived at the following conclusions: When acidified solutions of potassium permanganate are freed from oxide and agitated, there is no evolution of oxygen in measurable quantity if the acidity be not too great and the solutions not too concentrated, but even in a five per cent solution of permanganate, where the acidity was equivalent to three times the potassium present, the evolution in 150 hours only amounted to about 2 c.c.

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(1) Am. Chem. Jour. 18, 401.
(2) Ber 29: 2828.
(3) Am. Chem. Jour. XX. 521.

The reaction does not cease when the hydrogen has been wholly oxidized, whether the solutions be concentrated or dilute, although the rate of evolution becomes very much less after the first twenty-four hours are passed. For example: In a solution which after dilution with acid and water to fifty c.c. contained 20.4 m.g. of potassium permanganate per c.c. The evolution of oxygen resulting from the absorption of 40 c.c. of hydrogen in 24 hours amounted to 22.03 c.c. In 150 hours it increased to 26.67 c.c. and in 300 hours to 28.9 c.c. In more dilute solutions the ratio of increase after the first 24 hours was still greater. The authors did not determine the time required for the absorption of the hydrogen, and they worked at the temperature of the laboratory.

They suggested as the explanation of this evolution of oxygen that the molecules of manganese dioxide which are formed from the permanganic acid have a tendency to polymerize with the formation of much more complex molecules. In the use of gaseous reducing agents the molecules first formed are simple and hence tend strong-

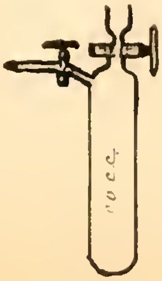
ly to polymerize at the expense of the permanganic acid. The chief evidence in favor of the complexity of the peroxide molecules is perhaps to be found in the large formulas which must be assigned to them in view of the small proportions of water of bases which they contain. "If they are thus complex, it is conceivable that the tendency toward increasing complexity of constitution ought to be strong enough to effect the decomposition of the permanganic acid with liberation of the superfluous oxygen". We would then assign the greater initial rapidity of evolution of oxygen to a greater initial simplicity of the oxide precipitated by the gaseous reducing agent.

The object of this work ~~then~~ is to investigate the evolution of oxygen observed when carbon monoxide is absorbed in an acidified solution of potassium permanganate with a view to obtaining evidence in regard to the above hypotheses.

DESCRIPTION OF APPARATUS.

The experiments were all carried out in a large air-bath which was kept at a constant temperature by means of a thermal regulator. A shaft kept revolving by means of a small electric motor was passed through the bath. The cylinders in which the solutions were confined were fastened upon this shaft by means of clamps in such a way that their centres revolved about a circle whose radius was nearly six inches. The solutions thus passed from one end of the tubes to the other twice for each revolution of the shaft which turned at a rate which varied slightly but approximated thirty-six revolutions per minute. The agitation thus secured was quite thorough and uniform. The temperature of the bath varied between 32-35° C., but was usually quite near to 35°.

The solutions subjected to examination were placed in cylinders which were fitted with two outlets. Its construction will be made plain by the figure.



The stop-cocks were gas tight. The larger one surmounted by a small funnel through which the solutions were introduced into and removed from the tubes. The smaller side tube was of thick-walled glass and nearly capillary bore.

Preparation of Materials.

The solutions of potassium permanganate used were of different strength and their concentration was determined by means of pure potassium tetroxalate. The solutions were purified in the manner described in the first part of this dissertation. The acid solutions and the water used were also prepared as previously described.

The preparation of the carbon monoxide was rendered easy, and its purity assured by means of a simple piece of apparatus. Two large nitrometers were used which were provided with Freidrich and Greiner stop-cocks. They were connected with each other by means of their side tubes, and the whole apparatus completely filled with mercury. One of the nitrometers had a capacity

of 150 c.c. The other of 50 c.c. Into the larger one was introduced a small quantity of concentrated caustic soda solution and into the other a few c.c. of concentrated sulphuric acid and a few drops of concentrated formic acid. All the air and a few c.c. of the gas first evolved were expelled through the stopcocks and the connection between the two nitrometers was opened. A large quantity of gas was thus prepared at one time and its purity was tested by absorption in ammoniacal cuprous chloride.

The Action of Carbon-monoxide on Acidified Solutions of Potassium Permanganate -

Carbon monoxide reacts upon potassium permanganate according to the following equation:

$$2\ KMnO_4 + 3\ CO = K_2CO_3 + 2\ CO_2 + 2\ MnO_2.$$

If the hypothesis of Morse and Reese is correct, then the simple molecules of manganese dioxide formed by the gaseous reducing agent have two means of satisfying their tendency to grow more complex by polymerization, 1) they may unite with each other or 2) they may decompose the permanganic acid with the consequent elimination of oxygen. If then we increase the propor-

tion of molecules of permanganic acid present in a given solution upon which a fixed number of molecules of carbon monoxide is allowed to act, then, according to the theory, we should expect the manganese dioxide to show an increased tendency to decompose the permanganic acid owing to the greater frequency of the permanganic acid molecules as compared with the manganese dioxide molecules. To test this we determined to use a fixed quantity of carbon monoxide and to vary the concentration of the solutions with which it was used.

Twelve cubic centimeters of gas under standard conditions was fixed upon as being suited to both strong and weak solutions and adapted to the size of the tubes.

By calculation on the basis of the above equation, it is found that 12 c.c. of carbon monoxide will reduce 56.44 m.g. of potassium permanganate to manganese dioxide, and at the same time be itself oxidized to carbon dioxide.

It was also desired to determine the time required for the complete absorption of this volume of carbon-

monoxide, for, in the light of the hypothesis previously mentioned, the rapid evolution of oxygen should not cease immediately upon the absorption of the gas.

The solutions used varied in concentration from one which contained 169.32 m.g. to one which contained 1749.64 m.g. of potassium permanganate, the volume being kept constant (50c.c.). A sufficient number of intermediate concentrations were used to bring out the differences shown. A detailed account of the method of work will be given for the most dilute solution which was employed.

A permanganate solution containing 6.85 m.g. per c.c. was prepared. Into one of the glass tubes previously described 24.72 c.c. (169.32m.g.) were measured. Sulphuric acid equivalent to the potassium of one-third and three times the potassium of the remaining two-thirds of the permanganate was then added together with sufficient water to make exactly 50 c.c. of solution. The tube was then placed in a clamp and by means of a Hempel burette about 16 c.c. of air was extracted through the side tube. The Hempel burette was then replaced by

a Lunge nitrometer containing carbon monoxide and from it the required amount of gas was measured into the tube. Of course corrections were made for the conditions under which the gas was measured. It should be noted that there is here an error equal to the volume of the passage of the stop-cock of the nitrometer to that of the tube. This volume is small, however, and of constant value throughout the experiments.

It will be seen that, if we consider the gas introduced to have acted <u>at once</u> upon the permanganate, the molecular proportions within the tube are now

$2\ HMnO_4 : MnO_2 : 2\ H_2SO_4 : 1\ 1/2K_2SO_4$.

The amount of potassium permanganate present in excess of that required ~~of~~ for the oxidation of the carbon monoxide is 112.88 m.g. (2 × 56.44). These proportions are expressed by the ratio 2:1. From this the meaning of the expressions 5:1, 10:1, 15:1, etc. will be plain. The dilution in every case being 50 c.c. It will be evident that, as the ratios increase, the concentration of the permanganate solutions and of the acid was also increased.

The tube being so filled was immediately placed upon the agitator within the bath and allowed to remain

until it was thought that the carbon-monoxide was nearly or quite gone. It was then removed, placed in a clamp with the side tube slightly elevated and connected with a nitrometer filled with mercury. The funnel was filled with pure water and a siphon connection made with a beaker of pure water. When the stop-cocks were opened, the gas was displaced by water and collected in the nitrometer without loss of permanganate and of but a small quantity of gas which necessarily remained in the neck of the tube. The gas was now analyzed by the Hempel method, and the amount of carbon-monoxide found was recorded. The solution was removed to a beaker and the amount of oxalic acid required to completely reduce the whole of the permanganate originally used was added to the tube together with a little sulphuric acid. The film of oxide being removed, the clear solution and repeated rinsings were poured into the beaker. ~~which~~ After having been slightly warmed, it was titrated to color with potassium permanganate. The amount required to restore color is of course equivalent to the reduction due to the gas plus any oxygen evolved. The amount due to the

gas was calculated according to the equation given on page 7, ~~keeping in mind~~ the fact being kept in mind that 1 c.c. reduced to MnO_2 is equal to 3/5 c.c. reduced to the manganous condition. The difference~~s~~ between this amount and that required to restore color is of course a measure of the oxygen evolved.

The results will be expressed in the amount of oxygen evolved as thus determined and in the percentage reduction to MnO_2 of the permanganic acid present in excess of that required for the oxidation of the carbon monoxide. To illustrate by an example: It was found that when the conditions were as above described there was no carbon monoxide remaining after eight hours of agitation. The amount of permanganate required to restore color was 5.23 c.c. which is equivalent to a reduction to MnO_2 of 5/8 X 5.23 - 871 c.c. Of this amount 8.24 c.c. were due to the oxidation of the carbon monoxide. The difference 0.47 c.c. 3/5 1.21 (since 1.c.c. of $K MnO_4$ containing 6.85 m.g. will evolve 1.21 c.c. of oxygen) is the volume of oxygen lost or 0.35 c.c. There were present 16.48 c.c. of $K MnO_4$ to be reduced to MnO_2,

Therefore the percentage reduction is 0.47 ÷ 16.48 = 2.85% For convenience the actual amount of permanganate used in each proportion will be given here. Since the volume of carbon-monoxide, the volume of the solution, and the relative quantity of acid remained constant, the only variable is the permanganate.

2:1.	3 × 56.44	=	169.32 m.g.
5:1	6 × 56.44	=	338.64 m.g.
7 1/2 :1	8 1/2 × 56.44	=	479.84 m.g.
10:1	11 × 56.44	=	630.84 m.g.
15:1	16 × 56.44	=	903.04 m.g.
20:1	21 × 56.44	=	1185.24 m.g.
25:1	26 × 56.44	=	1467.44 m.g.
30:1	31 × 56.44	=	1749.64 m.g.

In order to bring out some features of the work the experiments will be tabulated in two series. A. Those which relate to the time before and up to the complete absorption of the carbon-monoxide; and B. those which were agitated for different periods of time after the carbon-monoxide was known to be wholly absorbed.

Series A.

Ratio.	Time. hrs.	Oxygen evolved c.c.	CO found	Percentage reduction.
2:1	5.	.22	.85	1.76
	6.	.28	.60	2.25
	7.	.29	.35	2.51
	8.	.34	0.0	2.85
	8.	.34	0.0	2.85
5:1	2.	.73	1.65	2.39
	2.	.73	.95	1.41
	3.	.88	0.0	2.92
	3.	.88	0.0	2.92
10.1	1 1/2	1.65	.55	2.71
	1 1/2	1.40	.20	2.27
	2.	1.84	0.0	3.04
	2.	1.65	0.0	2.73
20:1	1.	2.80	2.6	2.31
	1.	2.80	.9	2.33
	1 1/2	3.33	0.0	2.77
	1 1/2	3.74	0.0	3.11

30:1	1.	5.27	.30	2.92
	1 1/4	5.36	0.0	2.98
	1 1/4	5.63	0.0	3.00

Series B. -

Ratio.		6 hr.			24 hr.			150 hr.	
		O.c.c.	%		O.c.c	%		O.c.c	%
2:1		CO not absorbed			.80	6.85		191	16.02
					.73	6.10		249	20.81
					.72	6.07			
					.71	5.95			
5:1	a	1.49	4.96	b	2.46	8.21	c	3.88	12.99
		1.35	4.46		2.30	7.64		3.88	12.99
7 1/2:1.	d	1.90	4.25	e	2.77	6.16	c	5.80	12.91
		1.90	4.25		2.77	6.16		5.96	13.25
	a	2.06	4.37	b	2.77	6.49			
		----	----		2.94	6.49			
10:1.	d	2.93	4.90	e	3.57	5.95	c	7.80	13.05
		2.93	4.90		3.57	5.95		----	-----
	f	3.20	5.34	g	3.84	6.43	h	7.80	13.05
		2.89	4.84		3.84	6.43		7.64	12.79
		3.20	5.34		3.87	6.49			
		3.13	5.21		4.14	6.87			
15:1.	f	3.84	4.21		5.26	5.78	h	9.54	10.47
		3.87	4.24		5.26	5.78		9.70	10.84

Ratio									
	b	4.79	3.99	g	5.89	4.89	l	10.75	8.86
		5.13	4.29		5.89	4.75		11.44	9.51
	i	5.10	4.24	k	5.30	4.38	h	10.81	8.99
		4.62	3.68		----	----		-----	----
		4.95	4.14		5.74	4.72		10.81	8.99
		5.30	4.38		5.89	4.90		11.03	9.18
25:1	i	5.90	3.92	k	6.06	4.02	l	13.66	9.09
		5.96	3.92		6.37	4.24		14.30	9.39
30:1	i.	6.38	3.53	k	7.48	4.15	l	15.25	8.46
		6.53	3.56		7.48	4.15		16.83	9.36
					7.32	4.06			

brace!

The experiments written within the same { were duplicates and those designated by the same letter were in the bath at the same time, and hence were probably more strictly comparable than those carried out at different times.

The following statement of the mean values derived from the results embodied in A. and B. may more clearly bring out the results.

Ratio of MnO$_2$ to MnO$_2$	Time of disappearance of the gas.	Oxy. evolved when the gas had just been absorbed.	Percentage reduction when gas had just disappeared	Agitation 6 hours.	
				Oxygen evolved c.c.	Percent-reduction
2:1	8 hr.	.34	2.85	---	---
5:1	3 hr.	.88	2.92	1.42	4.71
7 1/2:1	----	----	----	1.95	4.29
10:1	2 hr.	1.75	2.89	3.05	5.09
15.1	--	--	--	3.86	4.23
20:1	1 1/2 hr.	3.54	2.94	4.82	4.12
25:1	----	----	----	5.90	3.92
30:1	1 1/4 hr.	5.50	2.99	6.45	3.55

Agitation 24 hrs.		Agitation 150 hrs.	
Oxygen volved c.c.	Percent. reduction	Oxygen evolved c.c.	Per cent. reduction.
.74	6.24	2.20	18.42
2.38	7.93	3.88	12.99
2.81	6.24	5.88	13.08
3.81	6.35	7.75	12.99
5.26	5.78	9.62	10.66
5.71	4.73	10.97	9.11
6.22	4.13	13.98	9.24
7.43	4.12	16.04	8.91

- The absorption of carbon-monoxide by neutral permanganate and the oxygen evolved from solutions acidified after the gas had been observed.-

It was stated by V. Meyer and Recklinhausen(1) that, when hydrogen is absorbed by neutral permanganate, there is no evolution of oxygen such as is absorbed when the gas is absorbed in acidified solutions. It seemed to us that, if this were true for carbon-monoxide also, it would be of interest to determine whether the addition of acid after the disappearance of the gas would render this oxide active.

If the evolution of oxygen just discussed is ~~be~~ due to the polymerization of the molecules of the manganese dioxide at the expense of the permanganic acid, then it seems probable that the oxide formed in neutral solution could be rendered active by the addition of acid due to a change brought about in the oxide itself by the removal of a part of its base by the acid and to the formation of the less stable permanganaic acid from the permanganate.

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(1) Ber. 19, 2551.

That the results of such experiments may be comparable with those performed in the acid solutions it is necessary that the concentration of the solutions be equal after the acid had been added, and hence we were forced to absorb the gas in solutions of a concentration greater than the corresponding acid solutions by the amount of acid which was to be later introduced. It was of course necessary to use different quantities of acid in the various experiments, and for this reason the volume of the neutral solution employed in each case will be given.

Duplicate experiments were made in nearly every case in which no acid was introduced at any time, so that a check is furnished, and we are enabled to know whether the evolution of oxygen is due to the addition of the acid or to some other cause.

As before, the results are given in two series: A.- those which show the time required for the absorption of the gas, and B.- those which refer to the time after the solutions had been acidified.

The column headed "Reduction" gives in terms of

volume of oxygen the reduction in excess of what is required for the complete oxidation of the carbon monoxide, and where the values so obtained are negative they are indicated by a minus sign. It will be noted that in most cases the reduction is a little less than the amount required. The cause is probably to be found in the sources of error mentioned on pages 10 and 11.

In the second series (B) the acid was added immediately after the disappearance of the gas, and also after agitation had been continued in the neutral state for twenty-four hours. For this reason the time during which the solutions were agitated while neutral will also be given.

Series A.

Ratio of $HMnO_4$ to MnO_2	Vol. of Sol. c.c.	Time hr.	CO found c.c.	Reduction c.c. of O_2
2:1	47.54	5.	1.0	-0.08
		5	.85	-0.10
		9	.2	0.01
		9	.4	-0.01
		10.	0.0	-0.02
		10.	0.0	-0.01

5:1	44.94	3.	.6	-0.14
	.	3.	.2	-0.00
		4.	.2	-0.02
		4.	.4	-0.03
		5.	0.0	0.03
		5.	0.0	0.03
10:1	39.13	1 1/2	1.3	-0.13
		1 1/2	1.3	-0.13
		2.	0.0	-0.13
		2.	0.0	-0.26
20:1	41.25	1.	.4	-0.26
		1.	.9	-0.87
		1 1/2	.4	-0.7
		1 1/2	0	-0.00
		2	0	-0.00
		2	0	-0.53
30:1	37.24	1	.3	-0.09
		1	.2	-0.26
		1 1/4	0	0.17

Series B.

Ratio of H MnO_4 to MnO_2		Time neutral	in hrs. acid.	oxygen c.c.	Percentage reduction.
2:1.		(11	24	.89	7.34
		(11	24	.98	8.37
		(22	24	1.16	9.76
		(22	24	.98	8.37
		(26	24	1.06	8.92
		(26	24	1.14	9.65
		(13 1/2	150	5.67	47.51
		(13 1/2	150	5.66	47.39
5:1	a	(4	24	1.88	6.29
		(4	24	1.45	4.87
	a	(24	0.0	0.06	----
		(24	0.0	-0.11	----
	b	(24	24	1.68	5.67
		(24	24	1.74	5.84
	b	(48	00	0.06	----
		(48	00	0.06	----
		(4.	150	7.44	[illegible]
		(4	150	7.44	[illegible]

Ratio of $HMnO_4$ to MnO_2		Time in hrs. neutral:	acid	Oxygen c.c.	Percentage reduction.
10:1	c	(2	24	2.09	3.51
		(2	24	2.15	3.57
	c	(24	00	-0.13	---
		(24	00	-0.06	---
	d	(24	24	2.29	3.82
		(24	24	2.35	3.89
	d	(48	0.0	0.00	----
		(48	0.0	0.06	----
		3	150	11.40	18.83
		3	150	11.17	18.04
20:1	e	(1 1/2	24	3.46	2.84
		(1 1/2	24	3.54	2.94
	e	(25 1/2	00	0.13	----
		(25 1/2	00	0.07	----
	f	(24	00	0.00	----
		(24	00	-0.33	----
	f	(2	24	3.00	2.50
		(2	24	3.00	2.50
		(2	150	11.62	9.69
		(2	150	12.95	10.78

Insert page 24

see next sheet

Ratio of $HMnO_4$ to MnO	24 hr. Period				150 hr. Period.			
	Acid		Neutral		Acid		Neutral	
	0 c.c.	%	0 c.c.	%	0 c.c.	%	0 c.c.	%
2:1	.74	6.24	1.03	8.55	2.20	18.42	5.67	47.45
5:1	2.38	7.93	1.69	5.67	3.88	12.99	7.4[illegible]	2[illegible]
10:1	3.81	6.35	2.22	3.69	7.75	12.99	11.29	18.18
20:1	5.71	4.73	3.38	2.81	10.97	9.11	12.23	10.23
30:1	7.43	4.12	4.95	2.76	16.04	8.91	18.84	10.47

Conclusions.-

1. When carbon monoxide is absorbed in acid solutions of potassium permanganate the limit of the evolution of oxygen is not reached when the carbon monoxide has all been oxidized.

2. The rapid evolution of oxygen does not cease immediately after the disappearance of the gas, but the rate decreases gradually. In determining this fact two difficulties are encountered. It is impossible to determine the exact moment when all the gas is absorbed, and moreover the initial temperature of the solutions has

	g	(24	24	3.24	2.61
		(24	24	3.75	3.01
		(48	0.0	-0.06	----
		(48	0.0	0.06	----
		(2	24	3.34	2.77
		(2	24	4.06	3.33
30:1	h	(1 1/4	24	4.56	2.54
		(1 1/4	24	5.10	2.86
	h	(24	0.0	-0.09	-----
		(24	0.6	-0.17	----
	l	(24	24	4.74	2.62
		(24	24	5.42	3.01
	l	(48	0.0	0.35	----
		(48	0.0	0.52	----
		(2	150.0	18.40	10.10
		(2	150.0	19.27	10.84

The following table will express more clearly the relation volumes of oxygen evolved from solutions acidified before the introduction of the carbon monoxide and those where the acid was added subsequent to the absorption of the gas.

a considerable effect upon the rapidity of the absorption. The last traces of the gas disappear but slowly as will be apparent from a glance at the table on page 21 .

The validity of the above conclusion will be evident from the figures given in the following summary which expresses the volume of oxygen evolved per hour. These values are obtained by dividing the volume increments measured by the increment in time of agitation. The first column contains the volume of oxygen liberated per hour up to the time of the disappearance of the gas.

	8 hrs.	6 hrs.	24 hrs.	150 hrs.
2:1	0.0425	-------	.0250	.0116
5:1	3 hrs. 0.2933	.1800	.0533	.0129
7 1/2:1	-------	.3250*	.0477	.0164
10:1	2 hrs. .8750	.3250	.0422	.0297
15:1	-------	.6433*	.0777	.0346
20:1	1 1/2 hr. 2.36	.3940	.0495	.0417
25:1	------	.9500*	.0178	.0616
30:1	1 1/4 hr. 4.40	.2000	.0544	.0683.

* These values of course include the evolution during the

absorption of the carbon monoxide.

3. The rate of evolution of oxygen increases with the concentration of the permanganic acid, but this increase is not in direct proportion to the concentration as is shown by the decline in the percentage reduction.

4. The oxide formed in neutral solution is comparatively inactive in that condition, but becomes active upon the addition of acid.

The volume of oxygen evolved in twenty-four hours, after acidification by the reaction between the oxide and the permanganic acid, approaches more nearly that from similar solutions where the acid is present during the absorption of the carbon monoxide, as the dilution increases and becomes even greater where the conditions are in the series marked 2:1.

If the agitation ~~be~~ is continued a sufficient length of time, the volume of oxygen will in every case exceed that from the acidified solutions of correspond-

ing concentration.

That this oxide differs from that formed in the acid solution is not only apparent from its behavior in this respect, but also by the fact that it is much less compact and considerably lighter in color.

5. The remarkable liberation of oxygen when carbon monoxide is absorbed in acidified solutions of potassium permanganate is not due primarily to the carbon monixide, but is a secondary reaction between the permanganic acid and the manganese peroxide formed during the oxidation of the gas.

6. The hypotheses of Morse and Reese concerning the cause of these phenomena is supported by many of the facts brought out in this investigation. As has been stated, the hypothesis is that the reaction between the permanganic acid and the peroxides of manganese is due to the tendency of the peroxide molecules to grow more complex by polymerization, This tendency being strong

enough to decompose the permanganic acid with liberation of the superfluous oxygen, and that the remarkably rapid evolution of oxygen in the case of the absorption of carbon monoxide and of hydrogen is due to the greater initial simplicity of the oxide precipitated by these reagents.

The evidence in favor of this view may be recapitulated here.

That the oxides precipitated from permanganic acid by reducing agents is very complex in some cases is shown by the large formulas which must be assigned to them in order to account for the small amounts of bases and of water which they contain. Some of the many analyses of these oxides made in this laboratory are found in Chambers's Dissertation.(1) If these molecules are simple at the time of their formation they may be supposed to polymerize either with each other or with the oxide which they are able to obtain from the permanganic acid. The degree to which this latter reaction will take place depends upon the relative

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(1) Johns Hopkins, '96.

opportunities presented them for meeting molecules of permanganic acid as compared with other molecules of oxide. In other words it will depend on the concentration of the solutions used. We find such to be the case. On the other hand, the fact that the greater evolution in the more concentrated solutions is not directly proportional to the concentration is not surprising since the oxide is formed very much more rapidly and at the instant of formation may be supposed to have a much greater chance of being brought in contact with another molecule in a similar condition.

That the oxide grows less active as the time during which the reaction progresses is another point which is in accord with the hypotheses, for we conclude that as the molecules become more complex their affinity for other molecules becomes less marked.

The fact that agitation is necessary to secure the maximum evolution of oxygen may be considered as due to the great opportunity thus afforded to the molecules of oxide ~~for~~ to ~~coming~~ come in direct contact with

permanganic acid and also to the diminution of the probability of their union with each other.

The validity of the above reasoning may be tested by the following experiment which was not performed owing to lack of time. If the carbon-monoxide should be absorbed by being allowed to stand over an acidified solution of permanganate, the evolution of oxygen should be much less than when absorbed in a solution which is being agitated; and any subsequent agitation should only produce the comparatively slow evolution of oxygen which is noted after the first twenty-four hours of agitation. An indication of the probable result of such an experiment is to be found in the fact which was noted by Meyer and Recklinhausen (1) that when hydrogen is allowed to stand over acidified permanganate there is little or no evolution of oxygen.

It seems probable also that the fact that the oxide formed in neutral permanganate by the absorp-

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(1) Ber. XXIV., 2556.

tion of the gas is almost entirely unable to effect the decomposition of the permanganate, but becomes active upon the addition of acid is to be ascribed to two causes. It was shown in this laboratory (1) that, when potassium permanganate is decomposed by precipitated manganese dioxide, the oxide formed carries down with it almost all the base present. It is to be supposed therefore that upon the addition of acid the base thus precipitated would be partially removed by it, and the oxide become as a result capable of further polymerization which it is now able to accomplish at the expense of the less stable permanganic acid which has been formed at the same time.

This idea is also supported by some of the experiments recorded in the first section of this dissertation where it was found that, in general, those oxides which ~~were~~ are precipitated in neutral solution by liquid reducing agents ~~were~~ are more effective in producing the evolution of oxygen when acidified than those

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(1) Am. Chem. Jour. vol.XVIII. p.411.

formed in acid solution by the same reagents.

While it must be admitted that the evidence is not of such a nature as to amount to a demonstration of the truth of the hypothesis advanced, yet it lends to it an air of strong probability and points the way to a more thorough investigation of this very interesting reaction.

Biographical Sketch.

Horace G. Byers was born December 26, 1872, near Pulaski, Pennsylvania.

He entered the preparatory department of Westminster College in 1887 and, after an interval spent in teaching, graduated with the degree of A.B. and S.B. in 1895.

The following year he taught in Tarkio College, Missouri, and in January, 1897, entered the Johns Hopkins University. In 1898 he received the degree of Master of Arts from his Alma Mater. In January, 1899, was appointed a university scholar in Chemistry in the Johns Hopkins University.